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Fibre Labelling
Polytrimethylene terephthalate - PTT- DuPont

Intermediate report
Administrative Arrangement N. 2011- 32490
Analysis conducted on behalf of DG ENTERPRISE

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1. Abstract

In November 2011, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise to verify the validity and applicability of the testing methods, proposed by DuPont, for the identification and quantification of their new fibre polytrimethylene terephthalate (PTT). The fibre is a type of polyester that differs from the common one polyethylene terephthalate (PET) as it contains one more methylene group in the aliphatic chain that links the terephthalic moiety.

Experimental results confirmed that PTT can be identified using Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC). FT-IR is able to distinguish among the three types of polyester PTT, PET and polybutylene terephthalate (PBT), whereas DSC can differentiate only between PTT and PET on the basis of their melting points.

For quantification purposes, the normal pre-treatment described in the EU Regulation 1007/2011, was proved to be applicable to PTT and its correction factor b for mass loss during pre-treatment was established (0 %). This means that the novel fibre is completely insoluble when the normal pre-treatment is applied. The agreed allowance of the new fibre (which represents its humidity regain) was measured (0.34 %). The European network of national experts on Textile Labelling (ENNETL) established the value of 1.50 % for PTT agreed allowance, for consistency with the already established values for polyester and elastomultiester. The solubility properties of PTT were evaluated with 15 methods described in EU Regulation 1007/2011, all of them with the exception of one (method 12). The new fibre was insoluble in methods 1-11, 13 and 16. The d correction factors were established on the basis of the experimental work carried out by the JRC. The resulting values were:

- 1.00 for methods 1, 2, 3, 7 and 11;
- 1.01 for methods 4, 5, 9 and 10;
- 1.02 for method 13;
- 1.03 for methods 6, 8 and 16.

PTT was completely soluble in method 14, whereas it was partially soluble in method 15 that consequently cannot be used in the quantification of blends containing PTT.

For the quantification of PTT in binary mixtures, manual separation is an adequate technique, whenever applicable. The following chemical dissolution methods can also be used: 1-11, 13, 14 and 16.

The quantification results of binary mixtures PTT/PET obtained by DSC method, using calibration curves built up with PTT and PET manually extracted from the sample under evaluation, were in very good agreement with the reference ones obtained through manual separation. In fact, the differences expressed in terms of bias were in all cases lower than 1%. In these conditions, the DSC method can be judged accurate.

A consensus among the members of ENNETL was reached on the need to validate the new, if possible improved, DSC quantification method to be added to the Textile Regulation. Consequently, the JRC was entrusted to organise the validation exercise at European level according to ISO 5725:1994. The discussion concerning the name and the definition of this fibre would be held in the final ENNETL meeting, which will be organised in April-May 2013.

2. Introduction

In January 2011, E. I. du Pont de Nemours and Company (DuPont) submitted an application to the European Commission's Directorate General Enterprise for the establishment of a new generic fibre name under Directive 2008/121/EC on textile names [1], now substituted by the EU Regulation 1007/2011 [2]. The applicant requested a new classification to make possible the distinction between the novel fibre polytrimethylene terephthalate (PTT) and the common polyester usually made by polyethylene terephthalate (PET). This idea was supported by the claimed properties of PTT, which could be of importance to the general public, such as durability, resilience, easy care, dyeability, UV and bleach resistance, and in particular elasticity, softness and comfort-stretch properties. Under the current legislation, polytrimethylene terephthalate can be labelled with the name polyester, as chemically speaking it is a polyester and the polyester definition (fibre formed of linear macromolecules comprising at least 85 % (by mass) in the chain of an ester of a diol and terephthalic acid) applies. The applicant requested a new name with the following definition: "fibre formed of linear macromolecules comprising at least 85% (by mass) in the chain of an ester of 1,3-propane diol and terephthalic acid". The proposed name was triexta.

The application was evaluated on 25th May 2011 during a meeting of the Working Group on Textile Names and Labelling, composed of Member States' governmental experts. The following agreed set of criteria were used for the evaluation of the petition:

1. the new fibre should be radically different from other fibres by chemical composition and/or by manufacturing route and production process;
2. fibre characteristics can be taken into account, but need to be examined on a case by case basis;
3. the new fibre should be detectable and distinguishable from other fibres by standardised test methods;
4. consumer relevance should be shown by active commercial use of the fibre;
5. a new name is justified only if the fibre cannot be classified into existing groups.

Even though the first criterion is not fulfilled by PTT, the group considered that the application could be technically and experimentally evaluated on the basis of its fibre

characteristics. Therefore, it was judged that experimental work was needed to verify the applicability of the proposed analytical methods for identifying and quantifying PTT in blends. The work requires in particular validated test methods at EU level in order to enable market surveillance authorities in Member States to determine the composition of textile products containing the new fibre. A modification of the European legislation on Textile Names and Labelling (EU Regulation 1007/2011) would need subsequently to be prepared.

In November 2011, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise (DG ENTR) to conduct the experimental work to verify the validity and applicability of the testing methods proposed by the applicant for the identification and quantification of the new fibre (Administrative Arrangement between JRC and DG ENTR, JRC Ref. Contract n. 32490).

3. Background information

The work plan included the verification of the applicability of the pre-treatment described in the EU Regulation 1007/2011 to the novel fibre, the determination of the percentage mass loss due to pre-treatment (*b*), the *agreed allowance*, the solubility properties of PTT, with the determination of its correction factors *d*, and its mechanical and elastic properties, according the standardised methods. The most important issue concerned the verification of identification and quantification methods proposed by DuPont (based on microscopic and FT-IR analysis, chemical dissolution methods and Differential Scanning Calorimetry).

The JRC collaborated with the applicant to identify relevant samples for the experimental phase, taking into consideration possible range of compositions in blends. In view of the possible difficulties in the quantification of blends containing polyester (PET), binary mixtures with PTT/PET were judged as the most interesting ones. DuPont was asked to provide various samples of pure PTT, both yarns from bobbin and staple fibre, with different linear densities (expressed in dtex), together with binary and ternary mixtures with polyester, elastane, polyamide, cotton, wool and modal. Table 1 lists all samples received from DuPont. The samples used in this project were both yarns and fabrics, received by the JRC from end February 2012 until August 2012. Samples **293-297, 299 – 300,** and **317** were yarns from bobbin made of pure PTT, sample **301** was a fabric of pure PTT, while sample **299** was the only one made of staple fibre. Sample **316** was yarn from bobbin made of pure PET. All the binary and ternary blends provided were fabric.

[1] **dtex** is a unit to express linear density, numerically equal to the weight in grams of 10 000 meters of yarn, fibre or other textile strand.

Table 1: Samples received from DuPont.

JRC code	Composition	Sample type	Colour	Arrival date	Customer code	linear density dtex	Filament number
	Pure fibre						
293	100% PTT	yarn from bobbin	white	2012.02.23	PTT-001	81	72
294	100% PTT	yarn from bobbin	white	2012.02.23	PTT-002	56	34
295	100% PTT	yarn from bobbin	white	2012.02.23	PTT-003	78	34
296	100% PTT	yarn from bobbin	white	2012.02.23	PTT-004	83	72
297	100% PTT	yarn from bobbin	grey	2012.02.23	PTT-005	1379	70
299	100% PTT	staple fiber	white	2012.03.21	Triexta Fabric 4	1.7	
300	100% PTT	yarn from bobbin	white	2012.03.21	Triexta Fabric 5 PTT Fiber	55.6	24
301	100% PTT	woven, plain weave	brown	2012.03.21	Triexta Fabric 1	81	36
317	100% PTT	yarn from bobbin	white	2012.07.09			
316	100% PET	yarn from bobbin	white	2012.07.09			
	Binary Mixtures						
298	66% PTT - 34% PET	woven fabric	grey	2012.02.23	PTTPET-001		
302	65% PTT - 35% PET	woven, plain weave	grey	2012.03.21	Triexta Fabric 2	81	36
303	50% PTT - 50% PET	knit, mesh	pink	2012.03.21	Triexta Fabric 3	81	72
308	55% PTT - 45% PET	woven fabric	light blue	2012.06.14	Triexta Fabric 8		
309	75% PTT - 25% PET	woven fabric	grey	2012.06.14	Triexta Fabric 9		
310	70% PTT - 20% PET	woven fabric	black	2012.07.09	Triexta Fabric 10		
311	60% PTT - 40% PET	woven fabric	brown	2012.07.09	Triexta Fabric 11		
312	60% PTT - 40% PET	woven fabric	blue	2012.07.09	Triexta Fabric 12		
313	48% PTT - 52% PET	woven fabric	black	2012.07.09	Triexta Fabric 13		
315	21% PTT - 79% PET	woven fabric	black	2012.07.09	Triexta Fabric 15		
305	80% PTT - 20% Elastane	knit, warp knit	blue	2012.03.21	Triexta Fabric 5	55.6	24
306	41% PTT - 58% polyamide	woven fabric	purple	2012.06.14	Triexta Fabric 6		
314	30% PTT - 70% Cotton	woven fabric	white	2012.07.09	Triexta Fabric 14		
321	30% PTT - 70% Cotton	woven fabric	white	2012.08.28	Triexta Fabric 16		
323	40% PTT - 60% Cotton	knit	blue	2012.08.28	Triexta Fabric 18		
322	76% PTT - 24% Merino Wool	knit	grey	2012.08.28	Triexta Fabric 17		
	Ternary mixtures						
304	68% Modal - 28% PTT - 5% Elastane	knit, single jersey	black	2012.03.21	Triexta Fabric 4	38 mm staple	
307	76% PTT - 17% PET - 7% polyamide	woven fabric	black	2012.06.14	Triexta Fabric 7		
324	58% ProModal - 37% PTT - 5% Elastane	knit	red	2012.08.28	Triexta Fabric 19		

4. Test methods for identification and characterization of the new fibre

The methods proposed by the applicant for identifying PTT were based on visual and microscopic inspection, Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and mechanical properties analysis. In this section results obtained with these techniques are reported. It has to be highlighted that, due to its chemical composition, the new fibre has to be distinguishable in particular from other types of polyester, such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

4.1 Microscopy

The optical microscopic analysis of pure PTT and PET are shown in Figures 1 and 2, respectively. A Zeiss microscope model Axioskop 2 Mat was used and analyses were performed using transmitted light. Glyceryl triacetate (refractive index: 1.158) was used as mounting medium.

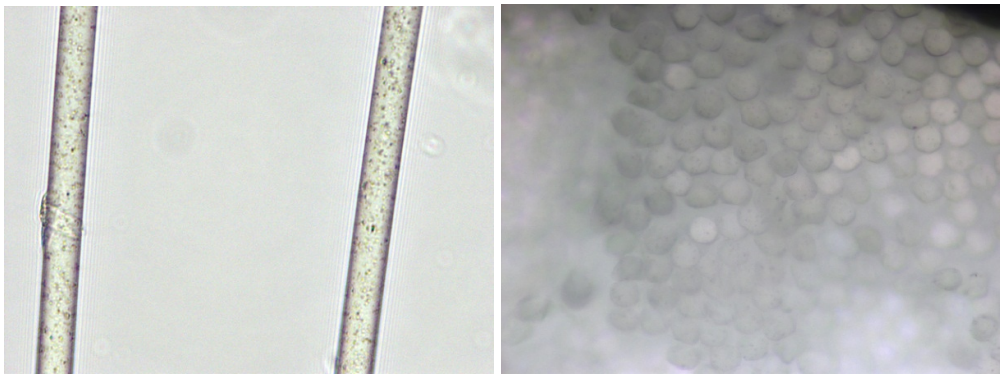

Fig. 1: Longitudinal and cross section analysis of PTT 500x and 400x (sample **294**).

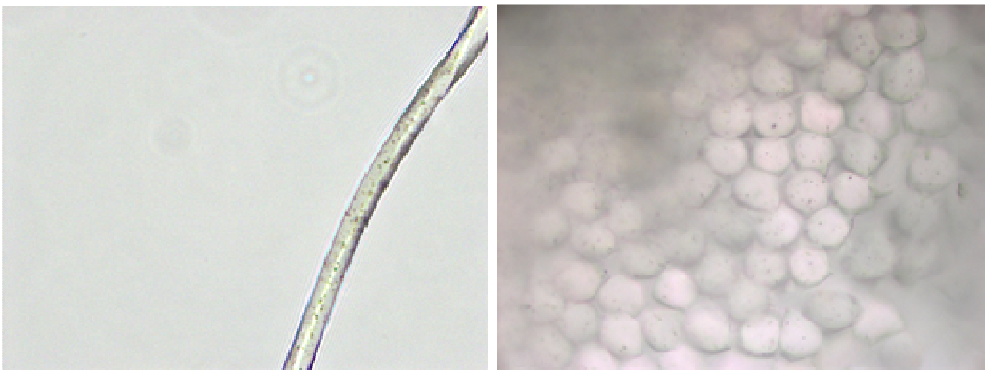

Fig. 2: Longitudinal and cross section analysis of PET 500x (sample **015**).

The cross-section of PTT fibre cannot be used for its identification as the fibre can be given a variety of cross section shapes, such as round, delta and trilobal. As evident from the photos reported as an example, PTT cannot be identified by optical microscopy since it has the same appearance as the most common polyester (PET), and other man-made fibres in general.

4.2 Fourier transform infrared spectroscopy

The nature of the new fibre can be identified by means of Fourier transform infrared spectroscopy (FT-IR). All spectra were acquired using Attenuated Total Reflectance (ATR) mode with a Perkin Elmer instrument (FT-IR spectrometer spectrum 2000). Spectra were acquired in the scan range 4000.00 - 530.00 cm^{-1}, with a resolution of 4.00 cm^{-1} and a total of 4 scans. The FT-IR spectra of pure PTT, PET and PBT (Figs. 3-5), as well as the overlay of the spectra combination PTT-PET, PTT-PBT and PET-PBT (Figs 6-8) are shown below. Samples were analysed without any preparation.

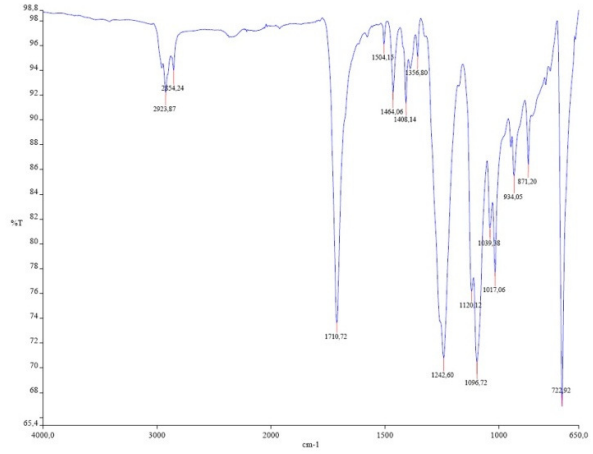

Fig. 3: FT-IR spectrum of PTT (sample **297**).

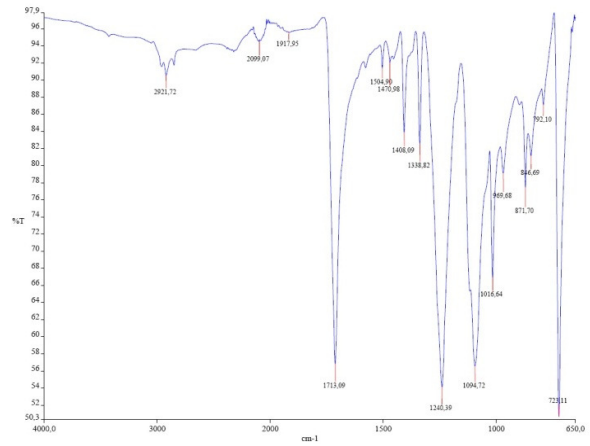

Fig. 4: FT-IR spectrum of PET (sample **015**).

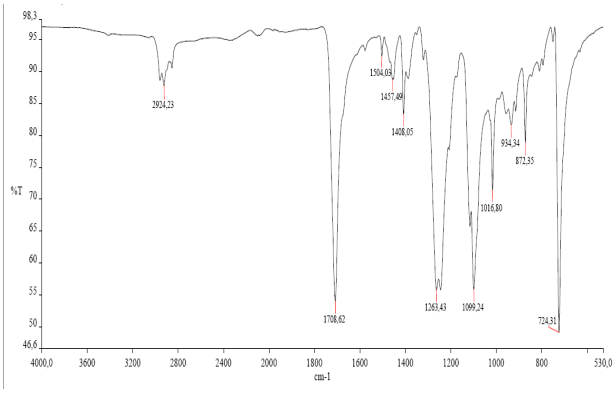

Fig 5: FT-IR spectrum of PBT (sample **086**).

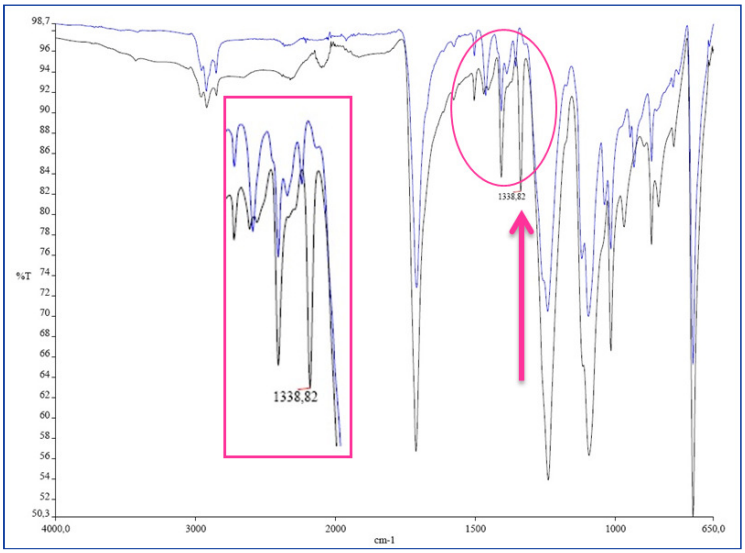

Fig. 6: Overlap of FT-IR spectra of PTT (blue – sample **297**) and PET (black - sample **015**); the pink box reports an expansion of the spectra main differences.

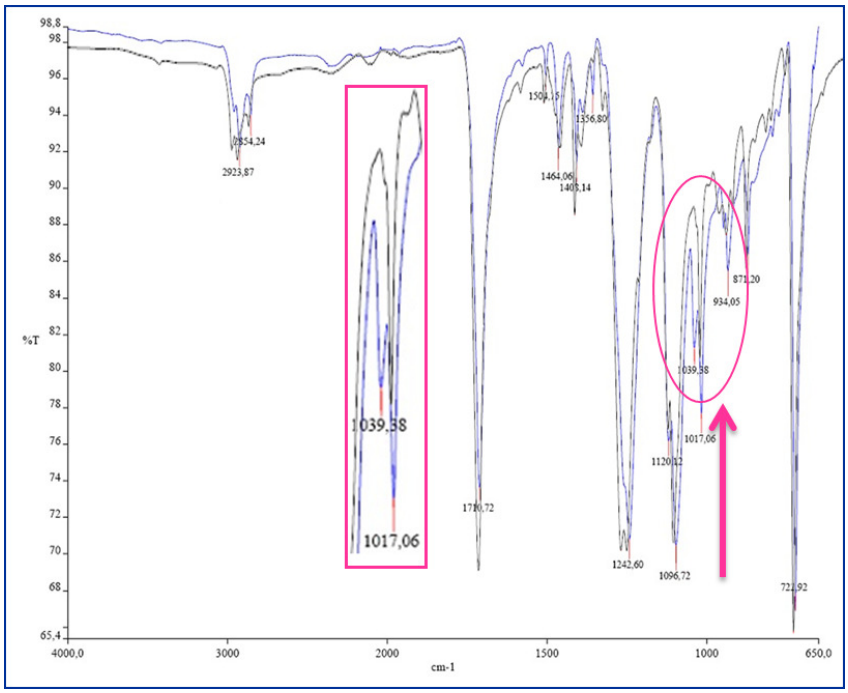

Fig.7: Overlap of FT-IR spectra of PTT (blue – sample **297**) and PBT (black - sample **086**); the pink box reports an expansion of the spectra main differences.

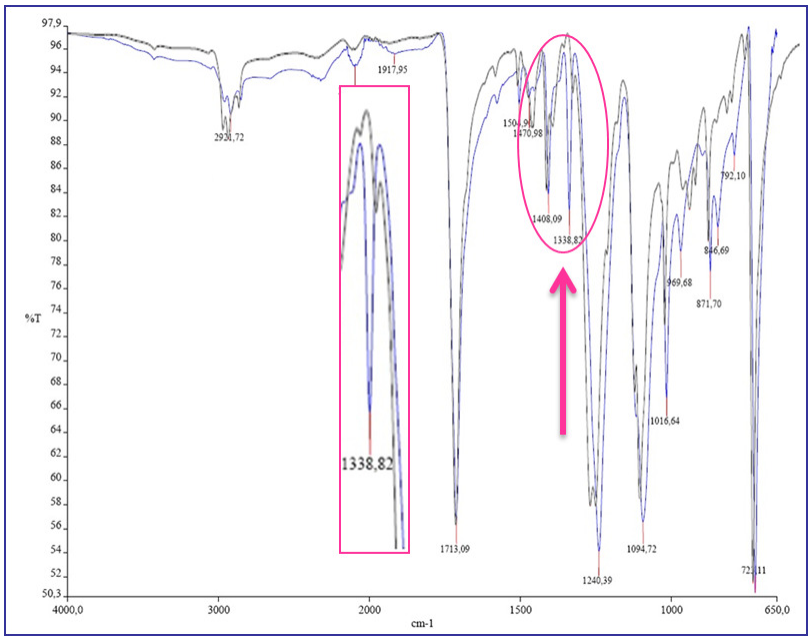

Fig. 8: Overlap of FT-IR spectra of PET (blue – sample **015**) and PBT (black – sample **086**); the pink box reports an expansion of the spectra main differences.

Due to the chemical composition of the novel fibre, PTT spectrum shows one strong peak attributed to its ester group (1711 cm^{-1}), which can also be seen in the spectra of both PET and PBT. Among the other main bands, common also to the other

polyesters PET and PBT, there is the one at 1465 cm^{-1}, which corresponds to the bending vibrations of methylene; the band at 1408 cm^{-1}, corresponding to the C-C stretching vibration in the benzene ring and the bands at 1017 and 723 cm^{-1}, which correspond to the bending vibration of the phenylic C-H bonds [3-4].

As evident from Figures 6-8, on one hand, PET can be distinguished from both PTT and PBT due to the presence of one peak at around 1339 cm^{-1} in its spectrum, which corresponds to the O-C-H bending vibration and is typical of the PET *trans* conformer. On the other hand, PTT spectrum shows one peak at 1039 cm^{-1}, which is absent in the PBT and PET spectrum. This peak corresponds to the C-C stretching mode of the PTT's three methylene units, which are arranged in a *gauche-gauche* conformation. As the methylene units of PET and PBT are arranged in different conformations (*trans-trans* and *trans-gauche-trans,* respectively) their spectra lack the 1039 cm^{-1} peak. Thus, FT-IR can be used to differentiate the three types of polyester.

4.3 Differential scanning calorimetry

On the basis of the different melting points, Differential Scanning Calorimetry (DSC) can also be used to distinguish between PTT and PET, whereas it fails to identify PTT in the presence of PBT.

The equipment used for the analyses was a DSC model Q100 by TA Instruments. A temperature program of 10 °C/min, starting from 42°C up to 300 °C, with a nitrogen gas flow of 50 ml/min was employed. The experimental method used consisted either in a heating - cooling - heating cycle or in a single heating cycle. Samples weight were in the range 4 - 10 mg. Fig. 8 shows the crystallisation and melting peaks of pure PTT, which appear at 161 °C and 224 °C (first heating) and 227 °C (second heating), respectively. Analogously, the crystallisation and melting peaks of pure PET were measured at 210°C and 254°C (first heating) and 255°C (second heating), respectively. For pure PBT only one heating cycle was performed and the melting peak was detected at 226°C, thus confirming that PTT and PBT show the same melting point.

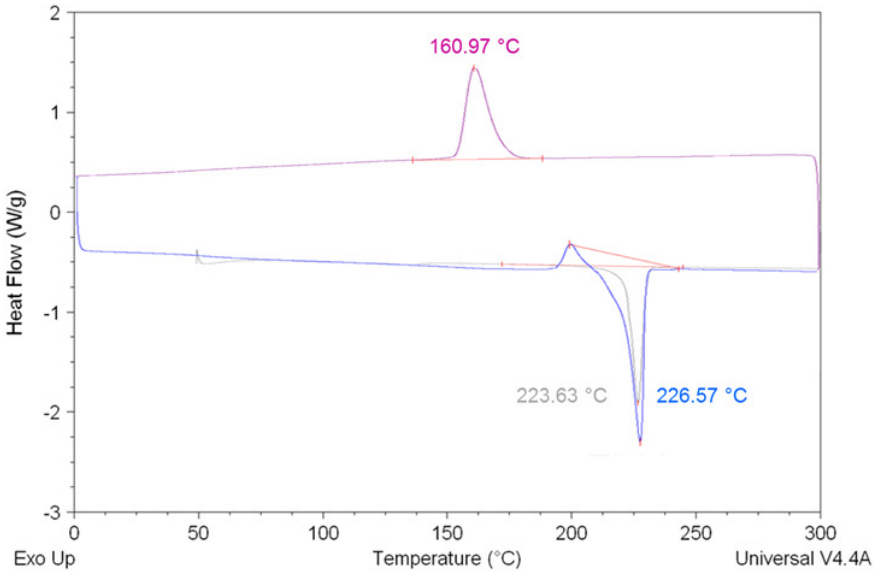

Fig. 9: DSC analysis of PTT (sample **296**).

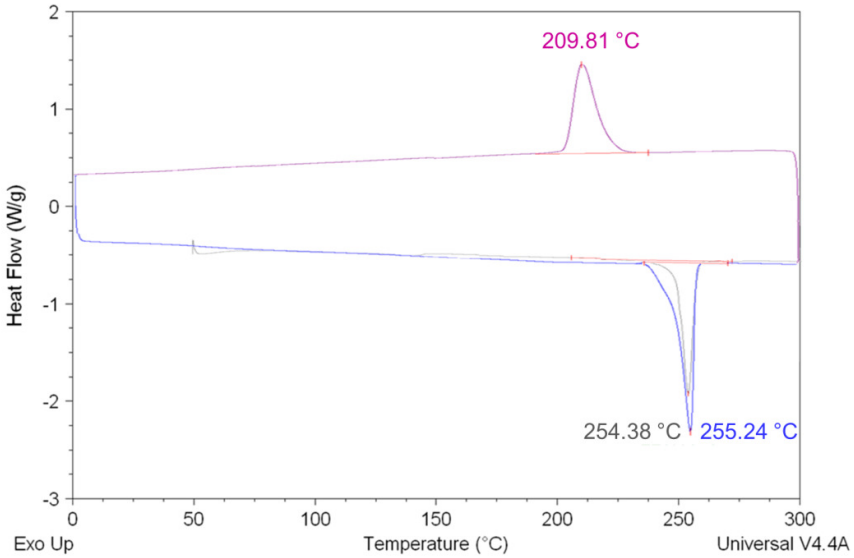

Fig. 10: DSC analysis of PET (sample **015**).

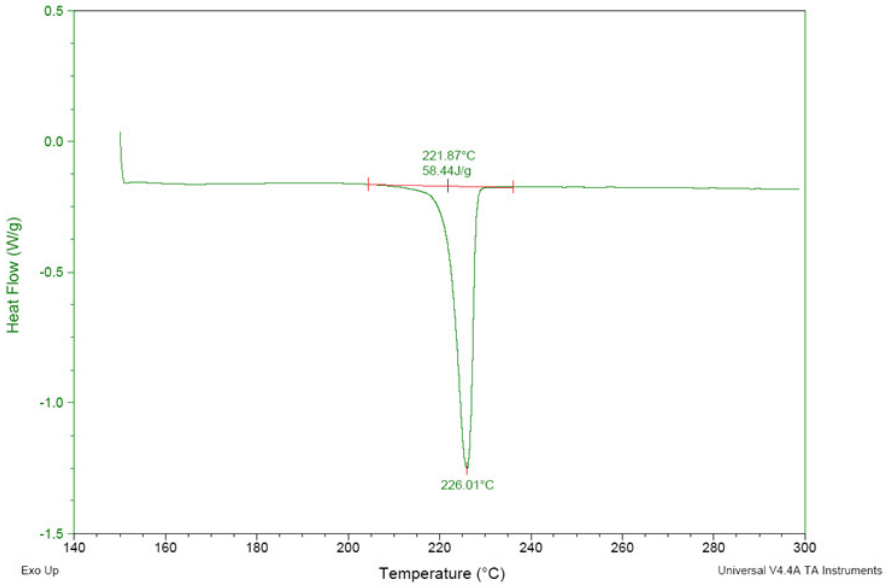

Fig. 11: DSC analysis of PBT (sample **086**).

4.4 Elongation at break

The method applied to determine the elongation at break of PTT yarns is described in chapter 6 (tensile properties) of the BISFA manual regarding test methods for bare elastane yarns [5]. The principle of this method foresees to mount a yarn specimen in the clamps of a tensile testing machine and to stretch it, at a constant rate of extension, until rupture. The breaking force, maximum load, per cent elongation at break and per cent elongation at maximum load were measured per each yarn sample on ten replicates.

An Instron dynamometer, model 5544 was used to perform tests with a clamping assembly with both flat jaws made of an alum alloy.

Fig. 12: Clamping assembly used for measurements.

A load cell of 50 N was used. The following test conditions were applied: speed of moving clamp 500 mm/min, pretension 0.001 ± 0.0001 cN/dtex, gauge length 50 ± 1.0 mm.

Before sampling yarns from bobbins, at least 100 meters from each package were removed and discarded. Before testing, all specimens were conditioned without any stress in standard atmosphere (21 ± 1°C, 65 ± 2 % relative humidity) for at least 16 hours.

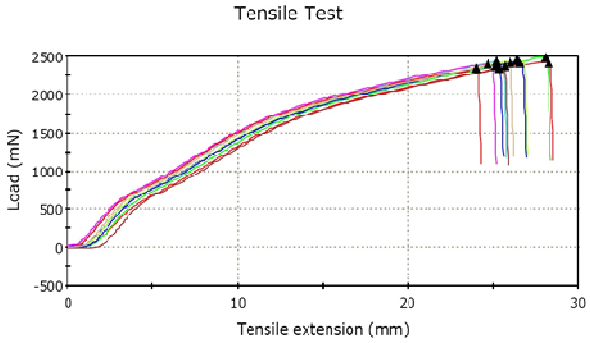

Fig. 13: Load versus extension curve (sample **293**, yarn).

Fig. 13 shows the trend of a typical curve load versus extension for PTT yarn, where the load continuously increases with extension until rupture.

Results reported in Table 2 suggested that the load at break of yarns depends on their linear density, the higher the linear density the higher the load at break. The results showed that it increased from 1490 to 7476 mN when the linear density augmented from 56 to 1379 dtex.

Table 2: Elongation at break of pure PTT yarns from bobbin.

JRC Code	Composition	dtex	filaments	dtex/filament	pret. (mg)	Repl.	Load at break (mN)	Elongation at break (%)
294	100% PTT	56	34	1.6	50	10	1490.8 ± 149.6	45.7 ± 3.1
300	100% PTT	56	24	2.3	50	10	1584.8 ± 52.2	63.7 ± 2.5
293	100% PTT	81	72	1.1	86	10	2408.7 ± 33.8	51.9 ± 2.0
295	100% PTT	78	34	2.3	86	11	2442.7 ± 80.6	32.9 ± 1.4
296	100% PTT	83	72	1.1	86	10	2395.7 ± 135.5	43.4 ± 2.0
317	100% PTT	81	unknown	unknown	86	10	2401.5 ± 60.1	44.8 ± 2.2
297	100% PTT	1379	70	20	1400	10	7476.2 ± 5656.1	129.8 ± 88.5

Some issues with repeatability of results were noticed in the case of sample **297**. Experimentally it could be noticed that the break of all the 70 filaments did not happen contemporaneously, as some filaments broke first and others subsequently, so

that the dynamometer did not record the break always at the same point of extension and load. This could be possibly due to the much higher value of linear density per filament of this sample (20 dtex/filament) in comparison with all the other samples (1.1-2.3 dtex/filament).

4.5 Elastic recovery

The standard method CEN 15930:2009 [6] regarding the elasticity of fibres was applied to evaluate the elastic properties of PTT yarns. This method covers the determination of recoverable stretch and permanent deformation of elastic yarns and is applicable to continuous filament yarns.

The same equipment, clamping assembly and load cell used to test the elongation at break was employed to determine the elastic recovery.

All pure PTT yarns from bobbin were tested. Also in this case, before sampling yarns from bobbin, at least 100 meters from each package were removed and discarded.

Before testing, specimens were conditioned without any stress in standard atmosphere (21 ± 1 °C, 65 ± 2 % relative humidity) for at least 16 hours. The following test conditions were applied: speed of moving clamp 50 mm/min, pretension 0.001 ± 0.0001 cN/dtex, gauge length 50 ± 1.0 mm. Load was set to zero after mounting specimens in the clamping assembly. Yarn extension was measured at pretension.

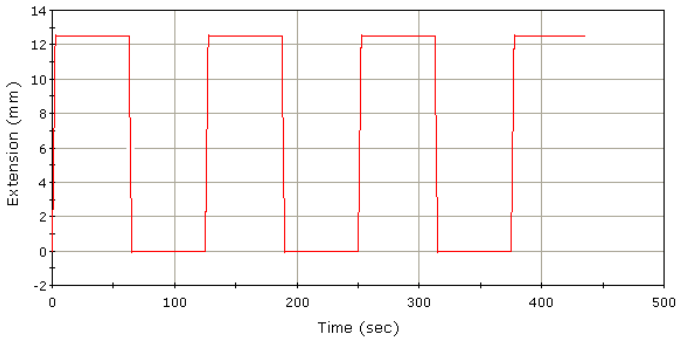

Fig. 14: Three-cycle method profile.

Fig. 14 reports the method profile. Specimens were extended to 12.5 mm (25% elongation) and were maintained at this elongation for one minute and then they were allowed to relax for one minute, after returning to the initial gauge length. The cycle was repeated two more times; finally specimens were extended again at the same per

cent elongation. Such a small elongation (25 %) was selected as the majority of PTT samples broke before reaching 50 % elongation.

Specimen extension was measured at pretension load on the fourth load cycle. Based on this measurement the per cent elastic recovery and permanent deformation (PD) of specimens were calculated (see equations 4.5.1 and 4.5.2).

$$elastic\ recovery - \frac{Espec - Erec}{Espec} \times 100 \qquad 4.5.1$$

$$permanent\ deformation = \frac{Erec}{Linit} \times 100 \qquad 4.5.2$$

where:

E_{spec} is the specified extension of the fibre, expressed in mm

E_{rec} is the extension determined at the specified pretension force on the fourth load cycle (recovery extension), expressed in mm

L_{init} is the initial length at the specified pretension on the first cycle, expressed in mm

As an example, the load versus extension curve obtained for a yarn is reported in Fig. 15.

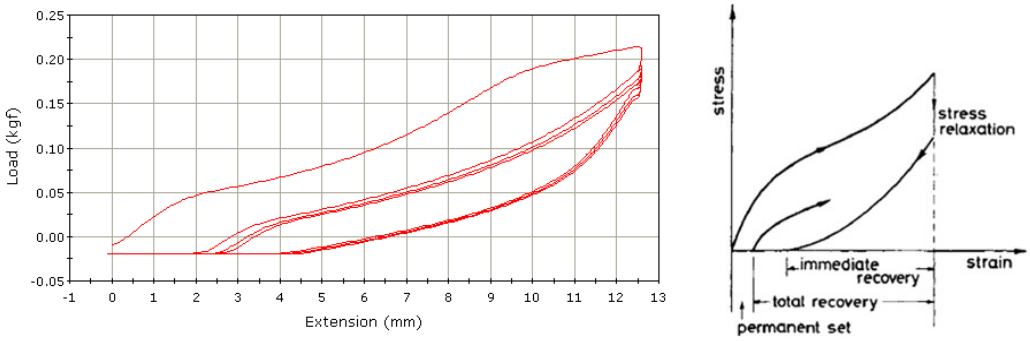

Fig. 15: Curve load versus extension for the three-cycle method based on elongation.

Table 3: Elastic recovery and permanent deformation of pure PTT yarns from bobbin.

JRC Code	Composition	dtex	pret. (mg)	replicates	Elastic recovery %	Permanent deformation %
293	100% PTT	81	86	12	84.64 ± 1.13	7.68 ± 0.57
294	100% PTT	56	50	10	87.56 ± 0.39	6.22 ± 0.19
295	100% PTT	78	86	10	86.59 ± 0.35	6.71 ± 0.18
297	100% PTT	1379	1400	10	82.33 ± 2.48	8.84 ± 1.24

Results regarding the elastic properties of PTT are reported in Table 3. The elastic recovery for PTT samples was in the range of 82.3-87.6%, corresponding to a permanent deformation of 6.2-8.8%. The elastic recovery did not seem to depend from the linear density of samples and it was quite good, but it has to be highlighted that the elongation was set at only 25 %.

5. Test methods for quantification of the new fibre

Initially, the JRC verified the applicability of the usual pre-treatment to the new fibre and determined both the mass loss due to pre-treatment and the *agreed allowance*. In a second phase, the behaviour of the new fibre was studied with all the methods described in the EU Regulation 1007/2011, with the exception of method 12 used for the determination of nitrogen content. This application of the various methods allowed the determination of the correction factors *d* for PTT for its mass loss. In a third phase, the DSC method proposed by the applicant for the quantification of blends PTT/PET was evaluated. Finally, all the samples made by binary and ternary mixtures received from DuPont (**298, 302-315, 321-324**) were analysed, if applicable, by manual separation, chemical analysis and DSC analysis.

5.1 Pre-treatment

Before quantification, samples should be pre-treated in order to eliminate non-fibrous matter. EU Regulation 1007/2011 suggests extracting non-fibrous matter with light petroleum ether and water. The procedure foresees one-hour extraction in Soxhlet with light petroleum ether (boiling range 40 - 60 °C), followed by one-hour extraction in water at room temperature and one-hour extraction in water at 65 ± 5 ºC, using a liquor/specimen ratio of 100/1. Both the traditional Soxhlet and an automatic hot-extractor (Soxhtec) were employed for the pre-treatment. No differences, both in terms of FT-IT spectra of the pre-treated samples and of mass loss, were noticed during preliminary experiments.

In order to evaluate the *b* coefficient for the new fibre (mass loss due to pre-treatment), the pre-treatment was carried out on six replicates, two grams each, of pure PTT (samples **296** and **293**). Results (Table 4) showed for sample **296** a mass loss of 0.73 ± 0.05 % and 0.63 ± 0.06 %, using Soxhlet and Soxhtec respectively (the confidence interval at 95 % probability is reported). The mass loss of sample **293** pre-treated in Soxhtec was 0.61 ± 0.07 %. Those values are in line with the content of finishing agents, in the range of 1.0 %, declared by DuPont. These results confirm that the new fibre is insoluble under the conditions of the pre-treatment. Therefore, in agreement with experts from Member States, the usual pre-treatment was considered applicable and the *b* coefficient value for PTT was established to be 0 %.

Table 4: Mass loss due to pre-treatment.

JRC Code	composition	description	replicates	mass loss (%)	conf. limit (95%)	method
296	100% PTT	yarn from bobbin 83 dtex	6	0.73	0.05	**Soxhlet**
296	100% PTT	yarn from bobbin 83 dtex	6	0.63	0.06	**Soxhtec**
293	100% PTT	yarn from bobbin 81 dtex	6	0.61	0.07	**Soxhtec**

Fig. 16 shows the comparison of FTIR spectra of PTT (sample **297**) as received and after pre-treatment.

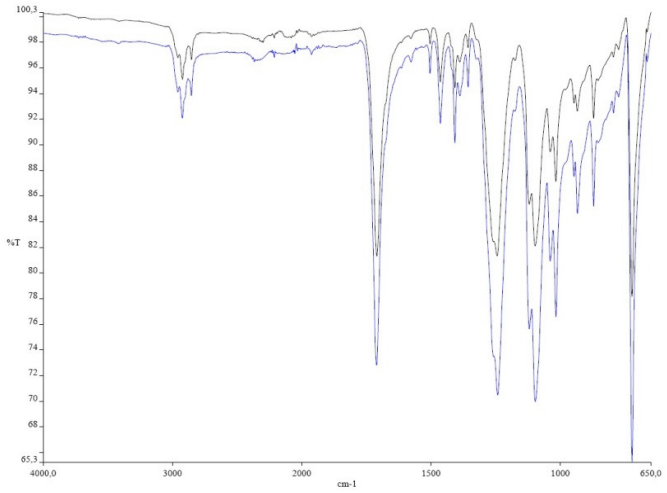

Fig. 16: Comparison of FT-IR spectra of untreated (---) and pre-treated (---) PTT (sample **297**).

5.2 Agreed allowance

The *agreed allowance* was considered equal to the moisture regain in standard atmosphere according to the definition stated in ISO 6348:1980 [7].

A number of experiments were performed on pure PTT, both yarn and staple fibre, (samples **296**, **297** and **299**) with different linear densities, in order to evaluate the *agreed allowance* of the new fibre. This parameter was calculated both for untreated and pre-treated samples. The procedure described in the following was applied. Weighing bottles were dried for 5 h at 105 °C, then cooled in a dessicator and weighed. A sample of about 2 g of PTT was placed in each weighing bottle and dried for 16 h at 105 °C, then cooled in a dessicator and weighed. Samples were then conditioned for 72 hours at 20 ± 1 °C and 65 ± 2 % relative humidity and weighed immediately after the conditioning period. The following formulas were used to calculate the *agreed allowance*:

water mass = wet sample mass – dried sample mass 5.2.1

agreed allowance = 100 (water mass / dried sample mass) 5.2.2

Ten replicates per each sample were analysed (Table 5). The untreated sample **296** was also analysed by DuPont on six replicates (it is reported as **296*** in Table 5). Results were similar for untreated and pre-treated samples and were in the range of 0.28 – 0.40 %, the average being 0.34 %.

Table 5: *Agreed allowance* (AA) for PTT.

				untreated sample		pre-treated sample	
JRC code	**Composition**	**Description**	**Repl.**	**AA (%)**	**Conf. limit (95 %)**	**AA (%)**	**Conf. limit (95 %)**
296	100% PTT	yarn - 83 dtex	10	**0.38**	0,04	**0.32**	0.04
297	100% PTT	yarn - 1379 dtex	10	**0.31**	0,04	**0.28**	0.03
299	100% PTT	staple fiber	10	**0.40**	0,03	**0.39**	0.03
296*	100% PTT	yarn - 83 dtex	6	**0.28**	0,03		
		average		**0.34**		**0.33**	
		overall average			**0.34**		

Even though the experimental value for PTT was 0.34 %, after discussions with experts from Member States, considering the established values for the *agreed allowances* of polyester and elastomultiester (both equal to 1.50 %) and the value proposed by DuPont (1.50 %), it was agreed to establish the same value of 1.50 % for the *agreed allowance* of PTT.

5.3 Solubility properties

The solubility properties of the novel fibre were studied and correction factors *d* for mass loss of the insoluble component in the reagents during analysis were evaluated, after pre-treatment. The correction factors *d* were calculated using the following formula:

$$d = \frac{m}{r} \qquad 5.3.1$$

where:

m is the dry mass of the specimen after pre-treatment

r is the dry mass of the residue

All weighing operations were performed using an analytical balance of weighing capacity of 0.01 mg. The percentages of insoluble component on a clean, dry mass basis, disregarding loss of fibre mass during pre-treatment, were calculated using the following formula:

$$P_1\ \%\ =\ \frac{100\ r\ d}{m} \qquad 5.3.2$$

where:

P_1 is the percentage of clean, dry insoluble component

m is the dry mass of the specimen after pre-treatment

r is the dry mass of the residue

d is the correction factor for loss of mass of the insoluble component in the reagent during analysis

In the case of binary mixtures, calculations of percentage of insoluble component on clean, dry mass basis, with adjustment by conventional factors (*agreed allowances*) and, where appropriate, correction factors b for loss of mass during pre-treatment, were performed using the following formula:

$$P_{1A}\ \%\ =\ \frac{100\ P_1\left(1+\frac{a_1+b_1}{100}\right)}{P_1\left(1+\frac{a_1+b_1}{100}\right)+(100-P_1)\left(1+\frac{a_2+b_2}{100}\right)} \qquad 5.3.3$$

where:

P_{1A} is the percentage of insoluble component, adjusted by *agreed allowances* and for loss of mass during pre-treatment

P_1 is the percentage of clean, dry insoluble component as calculated from equation 5.3.2

a_1 is the *agreed allowance* for the insoluble component (listed in Annex IX to the EU Regulation 1007/2011 on textile fibre names and related labelling and marking of the fibre composition of textile products)

a_2 is the *agreed allowance* for the soluble component (listed in Annex IX to the EU Regulation 1007/2011 on textile fibre names and related labelling and marking of the fibre composition of textile products)

b_1 is the percentage loss of insoluble component caused by the pre-treatment

b_2 is the percentage loss of soluble component caused by the pre-treatment

The percentage of the soluble component (P_{2A} %) was obtained by difference.

The coefficients *b* used in the calculations were: 0 % for polyester, elastane, polyamide, cotton, wool and modal (as pointed out in the EU regulation 1007/2011) and also for PTT. The *agreed allowances* used in the calculations were: 1.50 % for PTT, 1.50 % for elastane, 5.75 % for polyamide, 8.50 % for cotton, 18.25 % for wool, 13.00 % for modal.

The solubility properties of elastane were studied using methods 3, 4, 7, 8 and 14 as they were not known from EU Regulation 1007/201, with the aim to find methods that could be used to quantify the binary mixture PTT/elastane (sample **305**) and the ternary mixtures modal/PTT/elastane (samples **304** and **324**). In the case of samples containing elastane, the normal pre-treatment with light petroleum ether and water is not applicable. The pre-treatment applied foresaw the following procedure: one-hour extraction in Gyrowash at 40 °C with an aqueous solution containing 5 g/L of the standard soap (Heal's standard soap, without optical brightening agent suitable for ISO 105 Parts C01-C05), followed by rinsing with water, using a liquor/specimen ratio of 100/1.

In addition, pre-treated specimens of about 1 g of PTT were analysed with all the chemical methods (apart from method 12 for nitrogen content) described in EU Regulation 1007/2011.

For each sample 10 - 20 replicates were analysed. The data were collected and subjected to statistical evaluation. The results were first examined for evidence of outliers using Grubbs' statistical test, as laid down in ISO 5725 [8]. Only very few outliers were found and eliminated out of all measurements. The valid results were then subjected to a further statistical evaluation. The average and standard deviation (SD) of each set of data were calculated, as well as the relative standard deviation (RSD). The RSD was used to measure the dispersion of the distribution of test results in one laboratory: the lower the value of RSD, the better the repeatability of the method. The confidence intervals were calculated at 95 % probability, using the following formula:

$$\mu = x_m \pm \frac{t\ s}{\sqrt{n}} \qquad 5.3.4$$

where:

t is the value listed in the Student's *t*-distribution for a certain number of degrees of freedom and level of probability

s is the estimated standard deviation

μ is the true value

x_m is the average of experimental results

n is the number of measurements

An overview of results regarding the solubility properties of PTT and elastane is shown in Tables 6 and 7, respectively. Table 8 reports the results obtained for PTT in the DuPont's laboratories. The comparison among results obtained at the JRC and Dupont and the already established *d* correction factors for polyester and elatomultiester is reported in Table 9.

Table 6: Solubility properties of PTT.

JRC code	Method	Repl.	% PTT	Conf. limit (95%)	JRC results *d* factor	Conf. limit (95%)	rounded results
296	**1**	20	99.15	0.09	**1.009**	0.001	1.01
296	**2**	10	100.35	0.13	**0.997**	0.001	1.00
296	**3**	10	99.74	0.06	**1.003**	0.001	1.00
296	**4**	20	99.31	0.11	**1.007**	0.001	1.01
296	**5**	10	99.12	0.12	**1.009**	0.001	1.01
296	**6**	20	97.18	0.04	**1.029**	0.0004	1.03
296	**7**	10	99.71	0.09	**1.003**	0.001	1.00
296	**8**	10	96.94	0.11	**1.032**	0.001	1.03
296	**9**	10	99.03	0.06	**1.010**	0.001	1.01
296	**10**	10	99.32	0.08	**1.007**	0.001	1.01
296	**11**	10	99.61	0.10	**1.004**	0.001	1.00
296	**13**	20	98.09	0.04	**1.020**	0.0005	1.02
301	**14**	10	99.96	0.12	**soluble**		soluble
296	**15**	10	95.06	0.50	**1.052**	0.006	1.05
296	**16**	10	97.35	0.03	**1.027**	0.0003	1.03

Table 7: Solubility properties of elastane.

JRC code	Method	Repl.	% PTT	Conf. limit (95%)	JRC results *d* factor	Conf. limit (95%)	rounded results
95	**3**	10	99.57	0.08	**soluble**		
95	**4**	10	98.37	0.16	**1.017**	0.002	1.02
95	**7**	10	99.96	0.05	**soluble**		
95	**8**	10	100.03	0.04	**soluble**		
95	**14**	10	99.94	0.04	**soluble**		

Table 8: Solubility properties of PTT (DuPont results).

JRC code	Method	Repl.	% PTT	Conf. limit (95%)	DuPont results *d* factor	Conf. limit (95%)	rounded results
296	**1**	6	99.75	0.13	**1.002**	0.001	1.00
296	**2**	6	99.76	0.34	**1.002**	0.003	1.00
296	**3**	6	99.08	0.33	**1.009**	0.003	1.01
296	**4**	6	98.99	0.09	**1.010**	0.001	1.01
296	**5**	6	98.22	0.33	**1.018**	0.003	1.02
296	**6**	6	98.23	0.22	**1.018**	0.002	1.02
296	**7**	6	99.27	0.30	**1.007**	0.003	1.01
296	**8**	6	97.05	0.11	**1.030**	0.001	1.03
296	**9**	6	99.12	0.34	**1.009**	0.003	1.01
296	**10**	6	99.14	0.65	**1.009**	0.007	1.01
296	**11**	6	98.09	0.60	**1.020**	0.006	1.02
296	**13**	6	97.09	0.15	**1.030**	0.002	1.03
301	**14**	6			**soluble**		soluble
296	**15**	6	96.49	0.32	**1.036**	0.003	1.04
296	**16**	6	96.92	0.28	**1.032**	0.003	1.03

Table 9: Solubility properties of PTT, polyester and elastomultiester.

	PTT's experimental *d* factors		*d* factors established in Reg. 1007/2011	
Method	**JRC**	**DuPont**	**polyester**	**elastomultiester**
1	1.00	1.00	1.00	1.00
2	1.00	1.00	1.00	1.00
3	1.00	1.01	-	-
4	1.01	1.01	1.00	1.00
5	1.01	1.02	-	-
6	1.03	1.02	1.01	1.01
7	1.00	1.01	1.00	1.00
8	1.03	1.03	1.01	1.01
9	1.01	1.01	1.00	1.00
10	1.01	1.01	-	-
11	1.00	1.02	-	-
13	1.02	1.03	-	-
14	soluble	soluble	soluble	soluble
15	1.05	1.04	-	-
16	1.03	1.03	-	-

The correction factors *d* obtained by the JRC and DuPont were in good agreement. Out of 14 *d* factors newly determined, 7 were equal and the other 7 only slightly differed. Comparing the solubility properties of PTT, polyester and elastomultiester, PTT showed a slightly higher solubility in methods 4, 6, 8 and 9.

Polytrimethylene terephthalate is completely insoluble in methods 1-3, 7 and 11 (d = 1.00); it can be considered insoluble also in methods 4-6, 8-10, 13 and 16 (d = 1.01, 1.01, 1.03, 1.03, 1.01, 10.1, 1.02, 1.03, respectively); whereas it is partially soluble in method 15 (d = 1.05). PTT is completely soluble only in method 14 (concentrated sulphuric acid). Applying method 14 some difficulties were experienced when pure

PTT yarns were analysed. In fact, in this case, when the acid was added, the yarn sample was contracted and formed aggregates that could not be dissolved completely, unless a strong mechanical agitation was applied for the entire duration of the contact time (this was a deviation from the procedure described for method 14 which foresees to stir occasionally by hand). On the contrary, no problems were experienced when the method was applied to a pure PTT fabric, as in this case the normal procedure was able to dissolve completely the sample. Considering that, in general, enforcement laboratories would have to analyse the final consumer products, such as clothing that are in the form of fabric, no difficulties should be expected by the application of method 14.

The possible influence of various linear density and production process on the solubility properties of PTT was studied on methods 7 and 16, because they were considered the worst case scenario due their strong acid conditions (75 % sulphuric acid and 90 % formic acid, respectively) and high temperatures (50 °C and 90 °C, respectively). Method 7 was applied to all the pure PTT samples received (yarn, staple fibre and fabric). Results showed that in the range 1.7 – 1379 dtex there was not a clear difference and the average *d* correction factor for all sample was 1.00, as already measured on sample **296**. Apart from sample **296**, method 16 was also applied to sample **293**, which had shown the most different behaviour in the case of method 7. The *d* correction factors determined on these two samples were equal.

Table 10: Influence of linear density on solubility properties of PTT.

JRC code	Linear density dtex	Method	Repl.	% PTT	Conf. limit (95%)	*d* factors	Conf. limit (95%)	Rounded *d* factors
293	81	**7**	10	98.49	0.21	**1.015**	0.002	**1.02**
294	56	**7**	5	99.79	0.09	**1.002**	0.001	**1.00**
295	78	**7**	5	99.58	0.21	**1.004**	0.002	**1.00**
296	83	**7**	10	99.71	0.09	**1.003**	0.001	**1.00**
297	1379	**7**	5	99.54	0.09	**1.005**	0.001	**1.00**
299	1.7	**7**	5	99.46	0.12	**1.005**	0.001	**1.01**
301	81	**7**	5	100.26	0.14	**0.997**	0.001	**1.00**
317	unknown	**7**	5	99.25	0.13	**1.008**	0.001	**1.01**
300	56	**7**	5	99.77	0.14	**1.002**	0.001	**1.00**
			average			**1.004**		**1.00**
296		**16**	10	97.35	0.03	**1.027**	0.0003	**1.03**
293		**16**	10	97.12	0.04	**1.030**	0.0004	**1.03**
			average			**1.028**		**1.03**

In conclusion, blends containing PTT can be analysed with methods 1-11, 13 and 16 in which polytrimethylene terephthalate will remain as residue or with method 14 in which PTT is soluble. On the contrary, method 15 cannot be applied to mixtures containing PTT due to its partial solubility.

5.4 Quantification of binary and ternary mixtures containing PTT

5.4.1 *Manual separation*

When feasible, manual separation was performed on the binary and ternary mixtures in order to determine reference values against which results obtained with alternative methods were compared. In fact, this method is unanimously considered the most accurate one for the quantification of fibre blends.

Out of the ten binary mixtures PTT/PET available, six woven fabrics could be analysed by manual separation. However, despite the declared composition, one of them, sample **308**, resulted to be made of pure PTT. On the following binary blends PTT/PET (samples **303**, **310**, **313** and **315**), PTT/elastane (**305**) and PTT/cotton (**314**, **321** and **323**) manual separation was not applicable either because of the fabric construction or because the separated yarns were made by intimate mixture of the different fibres.

The values of *agreed allowance* used for the calculation of results were 1.50 % for PTT and polyester, 18.25 % for wool and 5.75 % for polyamide. Table 11 reports the quantification obtained by the JRC, on six or ten replicates, and by DuPont on three replicates. Results were in excellent agreement, confirming that the manual separation is a very accurate and reproducible method.

Table 11: Quantification of binary mixtures (manual separation).

			JRC results			DuPont results		
JRC code	**Declared Composition**	**Sample type**	**Repl.**	**% PTT**	**Conf. limit (95%)**	**Repl.**	**% PTT**	**Conf. limit (95%)**
298	66% PTT - 34% PET	woven fabric	6	**66.33**	0.13			
302	65% PTT - 35% PET	woven fabric	10	**74.14**	0.07	3	**74.26**	0.17
309	75% PTT - 25% PET	woven fabric	10	**76.06**	0.05	3	**76.11**	0.04
311	60% PTT - 40% PET	woven fabric	10	**70.32**	0.08	3	**70.34**	0.33
312	60% PTT - 40% PET	woven fabric	10	**62.95**	0.2	3	**62.89**	0.03
306	41% PTT - 58% polyamide	woven fabric	6	**43.37**	0.39			
322	76% PTT - 24% wool	knitted fabric	10	**77.38**	0.15			
307	76% PTT - 17% PET - 7% polyamide	woven fabric	6	**76.51**	0.08			

5.4.2 *Chemical analysis*

Binary mixtures of PTT/PET could not be quantified by any chemical methods as the solubility properties of these two fibres are practically identical. Method 7 was used to quantify the binary mixtures PTT/cotton and PTT/elastane, method 4 for the blends PTT/polyamide and method 2 for PTT/wool. In all these method PTT was insoluble. Results are reported in Table 12, together with the trueness of method 4 and 2. The trueness of method 4 and 2 (expressed as bias) was calculated for samples **306** and **322**, as the difference between the content of PTT (%), obtained by method 4 or 2, and its reference value, obtained by manual separation. In fact, trueness, as defined in ISO 5725 – Part 1, is the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value. It is usually expressed in terms of bias, which is the difference between the expectation of the test results and an accepted reference value. The quantification made by the chemical methods 4 and 2 was in very good agreement with the reference values obtained via manual separation, thus confirming the accuracy of these methods.

Sample **307**, ternary mixture of PTT, polyester and polyamide, could not be fully quantified, as no chemical method is available for blends made by PTT and PET. In this case, only the percentage of polyamide could be determined by dissolving it with method 4, based on 80 % formic acid aqueous solution.

Samples **304** and **324**, ternary mixtures of PTT with modal and elastane, were quantified, but the accuracy of the methods used could not be measured as the manual separation of these two samples was not feasible (Table 13). The content of PTT, however, is in the range of the declared composition.

The *agreed allowances* used in the calculations were: 1.50 % for PTT, 1.50 % for elastane, 5.75 % for polyamide, 8.50 % for cotton, 18.25 % for wool and 13.00% for modal. According to the analysis performed on PTT samples (Tab. 6), the *d* factor used for methods 2, 4 and 7 were 1.00, 1.01 and 1.00, respectively.

Table 12: Quantification of binary mixtures containing PTT by chemical methods.

JRC code	Declared Composition	Manual sep. % PTT	Method	Repl.	Chem. meth. % PTT	Conf. limit (95%)	Bias
305	80% PTT - 20% elastane	-	7	10	**84.10**	0.14	-
306	41% PTT - 58% polyamide	43.37	4	6	**43.11**	0.33	**-0.26**
322	76% PTT - 24% wool	77.38	2	10	**77.39**	0.13	**0.01**
314=321	30% PTT - 70% cotton	-	7	10	**29.30**	0.06	-
323	40% PTT - 60% cotton	-	7	10	**42.05**	0.15	-

Table 13: Quantification of ternary mixtures containing PTT by chemical methods.

JRC code	Declared Composition	Method	% PTT	% Modal	% Elastane
304	68% modal - 28% PTT - 5% elastane	7,8	**25.31**	70.87	3.82
324	58% modal - 37% PTT - 5% elastane	7,8	**39.03**	59.23	1.74
			% PTT + PET	**% Polyamide**	
307	76% PTT - 17% PET - 7% polyamide	4	92.98	7.02	

5.4.3 *DSC method*

The analyses were performed using a Differential Scanning Calorimeter from TA Instruments, model Q100, equipped with an auto sampler. The analysis foresaw heating-cooling-heating cycles with the following temperature program: 42 °C – 10 °C/min – 300 °C – 10 °C/min – 0 °C – 10 °C/min – 300 °C. The nitrogen gas flow was set at 50 ml/min, and the weight of samples was in the range 2-10 mg.

Usually with DSC the first heating cycle is used to erase the thermal history of samples and the melting peaks are integrated on the second heating. However, with PTT samples the melting peaks in the second heating cycle were misshaped and their integration was not repeatable; for this reason it was decided to integrate the enthalpy of fusion of the melting peak on the first heating cycle. In order to quantify PTT/PET binary mixtures, a calibration curve was built up using handmade independent mixtures containing various percentages of PTT and PET. The samples used as standards were **296** for PTT and **015** for PET. The calibration curve was linear and showed a good correlation factor (Fig. 17).

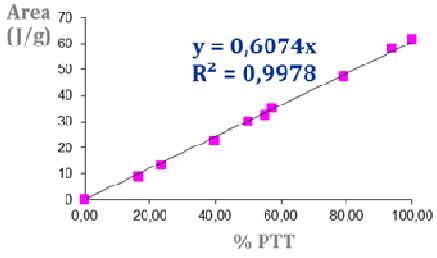

Figure 17: Calibration curve built up with samples **296** (PTT) and **015** (PET).

Table 14 reports the quantification results of binary and ternary mixtures obtained using manual separation, chemical methods and DSC method. The values obtained via manual separation or, when not feasible, via chemical methods were considered reference values against which the trueness of the DSC method was measured. The

differences - expressed in terms of bias - were generally much higher than 1%, meaning that the DSC method was not accurate.

Table 14: Quantification of mixtures by DSC method (calibration curve **296/015**).

JRC Code	Declared Composition	% PTT MS	% PTT CM	calcurve 296 PTT/015 PET % PTT	bias (MS/CM) %
298	66% PTT - 34% PET	66.33	nd	65.81	-0.52
302	65% PTT - 35% PET	74.14	nd	76.07	1.93
303	50% PTT - 50% PET	nd	nd	29.53	
308	55% PTT - 45% PET (100% PTT)	100	nd	102.63	2.63
309	75% PTT - 25% PET	76.06	nd	78.66	2.60
310	70% PTT - 30% PET	nd	nd	70.00	
311	60% PTT - 40% PET	70.32	nd	73.75	3.43
312	60% PTT - 40% PET	62.95	nd	66.52	3.57
313	48% PTT - 52% PET	nd	nd	45.97	
315	21% PTT - 79% PET	nd	nd	58.89	
305	80% PTT - 20% elastane	nd	84.1	80.63	-3.47
314	30% PTT - 70% cotton	nd	29.3	31.00	1.70
322	76% PTT - 24% wool	77.38	77.39		
323	40% PTT - 60% cotton	nd	42.05		
304	68% modal - 28% PTT - 5% elastane	nd	25.31	26.80	1.49
324	58% modal - 37% PTT - 5% elastane	nd	41.98		

In order to verify if some differences existed among all the pure PTT samples available, they were analysed and their melting peaks, on the first heating, integrated. As reported in Table 15, various PTT samples showed different fusion enthalpies and the samples seemed to belong to three different groups. Group I which showed an average area of the melting peak equal to 64.32 J/g, group II with 61.78 J/g and group III with 59.59 J/g.

Table 15: DSC analysis of 100% PTT samples.

Groups	JRC Codes	repl.	Area J/g	SD J/g	Conf. limit (95%)
I	**293**	3	64.37	0.11	0.27
	294	3	64.21	0.09	0.21
	295	3	64.36	0.06	0.14
II	**296**	3	61.78	0.51	0.43
	297	3	61.43	0.09	0.23
	299	3	61.90	0.08	0.2
	317	3	61.94	0.,05	0.13
III	**300**	3	59.59	0.16	0.4

The t-Student test was applied to the average areas of the three groups to judge if they could be considered equal or not. The null hypothesis assumed that the three groups (compared two by two each time) showed the same average area. First of all, the standard deviations of the two independent sets of measurements under evaluation (s_1 and s_2, with the number of replicates $n_1 = n_2$) were analysed with the *F*-test (two-sided test) to determine if they differed significantly [9].

To check the variances, the statistic *F* was calculated:

$$F = \frac{s_1^2}{s_2^2} \qquad 5.4.3.1$$

where s_1^2 is the bigger variance, as *F* must be higher than 1.

Taking into consideration the degrees of freedom for each set of measurements and the confidence level required (95 % probability), *F* values were compared with the critical value $F_{n1-1,\ n2-1}$ (P=0.05) reported in tables. If the *F* value was higher than *F* critical, it was assumed that there was a statistically significant difference between the two variances.

To judge if the averages of two independent sets of measurements differed significantly, in the case of non-significant difference between variances, the statistic *t* was calculated as follows:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad 5.4.3.2$$

where $\bar{x}_1$ and $\bar{x}_2$ are the sample means and n_1 and n_2 the number of replicates for the two sets of measurements. The degrees of freedom of *t* are $n_1 + n_2 - 2$.

The standard deviation was calculated with the following formula:

$$s^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{(n_1 + n_2 - 2)} \qquad 5.4.3.3$$

If the difference between variances was significant, then the statistic *t* was calculated as follows:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \qquad 5.4.3.4$$

with the degrees of freedom estimated using the Welch-Satterthwaiteu approximation:

$$\nu = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1 - 1)} + \frac{s_2^4}{n_2^2(n_1 - 1)}\right)} \qquad 5.4.3.5$$

When necessary, the calculated value of ν was rounded down to the nearest integer.

Finally, t values were compared with the critical value t (P=0.05) reported in the Student's t-distribution tables. According to the t-test, the difference between the two averages could be considered not significant when the calculated $|t|$ value did not exceed the critical one.

The overview of results is shown in Tables 16 and 17. The statistical analysis confirmed, at 95 % probability, that the average melting peak areas of the three groups of PTT samples were significantly different.

Table 16: Average melting peak areas for the three groups of pure PTT.

Groups	repl.	average area J/g	SD J/g
I	9	64.32	0.11
II	17	61.78	0.38
III	3	59.59	0.16

Table 17: Comparison of average melting peak areas for the three groups of pure PTT.

Groups	F	F crit (95%)	SD	T	T crit (95%)	average
I-II	12.67	4.07	≠	-25.694	2.086	≠
I-III	2.23	6.06	=	-59.248	2.228	≠
II-III	5.69	39.43	=	9.552	2.101	≠

Given the fact that statistically significant differences were observed among samples of pure PTT analysed as received on the first heating cycle, the samples were heat treated for 16 hours at 105 °C in a ventilated oven in order to try to erase their thermal history and to have the same degree of cristallinity in all PTT fibre samples. Sample

293 from the first group and samples **296** and **317** from the second one were studied. Results are reported in Table 18.

Table 18: DSC analysis of 100% PTT samples before and after heat treatment.

JRC Code	replicates	Area J/g	SD J/g
293	3	64.37	0.11
293 heat treated	3	63.41	0.04
296	8	61.78	0.51
296 heat treated	3	59.92	1.61
317	3	61.94	0.05
317 heat treated	3	61.85	0.12

Table 19: Comparison of average melting peak areas before and after heat treatment of samples.

JRC Code	F	F crit. (95%)	SD	T	T crit. (95%)	average
293	7.15	39.00	=	14.615	2.775	≠
296	9.97	6.54	≠	1.434	4.303	=
317	4.75	39.00	=	1.228	2.775	=

The t-Student test was applied to judge if the average melting peak areas before and after heat treatment could be considered equal or not. As reported in Table 19, the null hypothesis (meaning that the results obtained before and after heat treatment are equivalent) could be assumed for samples **296** and **317** at 95 % probability. However, this was not the case for sample **293**. Results were controversial as they did not clearly show if the heat treatment had an influence on the melting peak of PTT samples. Due to this uncertainty, three calibration curves were built up using handmade independent mixtures containing various percentages of PTT and PET. The samples used as standards, heat treated for 16 hours at 105 °C in a ventilated oven, were **293**, **296** and **317** for PTT and **316** for PET (Table 20).

Table 20: DSC calibration curves made with heat treated PTT and PET samples.

PTT Code	PET Code	m	R^2	points
296	316	0.5910	0.9968	8
317	316	0.6034	0.9979	8
293	316	0.6150	0.9962	7

Even though the three calibration curves were linear, they showed different angular coefficients which were the reason for the different quantification obtained for

mixtures containing PTT (Table 21). Results proved that, even applying the heat treatment to both standards and samples under quantification, the differences of the PTT content obtained via manual separation or chemical methods and the DSC method - expressed in terms of bias - were generally much higher than 1%, meaning that the DSC method was not accurate.

Table 21: Quantification of mixtures by DSC method (calibration curve with heat treated samples).

			Cal. Curve 296/316		Cal. Curve 317/316		Cal. Curve 293/316	
JRC Code	PTT % MS	PTT % CM	PTT %	bias % (MS/CM)	PTT %	bias % (MS/CM)	PTT %	bias % (MS/CM)
298	66.33	nd	68.00	1.67	66.60	0.27	65.40	-0.93
302	74.14	nd	70.15	-3.99	68.71	-5.43	67.41	-6.73
303	nd	nd	20.93		20.50		20.11	
308	100	nd	102.98	2.98	100.86	0.86	98.96	-1.04
309	76.06	nd	72.76	-3.30	71.26	-4.80	69.62	-6.14
310	nd	nd	62.62		61.34		60.18	
311	70.32	nd	68.88	-1.44	67.47	-2.85	66.20	-4.12
312	62.95	nd	59.46	-3.49	58.24	-4.71	57.14	-5.81
313	nd	nd	44.57		43.65		42.83	
315	nd	nd	57.46		56.28		55.22	
305	nd	84.1	78.00	-6.10	76.40	-7.70	74.96	-9.14
314	nd	29.3	29.75	0.45	29.13	-0.17	28.59	0.71
322	77.38	77.39	67.17	-10.21	65.79	-11.59	64.55	-12.83
323	nd	42.05	42.89		42.01		41.22	
304	nd	25.31	25.48	0.17	24.96	-0.35	24.49	-0.82
324	nd	41.98	37.60		36.82		36.13	

All results presented so far indicated the existence of various groups of PTT samples which showed different melting peak areas on the first heating cycle. To check if these differences were real or if they could be explained by lack of repeatability of the analysis and the peak integration, one sample from each group was analysed in five different days over three weeks, after being heat treated for 16 hours at 105 °C in a ventilated oven. The chosen samples were **293**, **296** and **300**, representing the three groups. Statistics (*F* and *t*-test) was used once more to compare the melting peak average area for each sample on different days. Results are reported in Tables 22-27.

In the case of samples **296** and **300**, a good repeatability was observed, as respectively in 8 and 7 comparisons out of 10 the averages could be considered statistically equivalent, at 95 % probability. This improves up to 10 and 9 comparisons out of 10, respectively, at 99 % probability. For sample **293** results showed lower repeatability; in fact, in 4 or 6 comparisons out of 10 the averages could be considered statistically equivalent, at 95 % or 99 % probability, respectively.

Table 22: Average melting peak areas of the heat treated sample **293** in different days.

JRC Code	day	replicates	Area J/g	SD J/g
	1-Wed week 39	10	60.89	0.57
	2-Mon week 40	10	59.91	0.67
293	3-Tue week 40	10	61.21	0.79
	4-Wed week 40	10	60.34	0.96
	5-Mon week 41	10	59.57	0.44

Table 23: Average melting peak areas of the heat treated sample **296** in different days.

JRC Code	day	replicates	Area J/g	SD J/g
	1-Wed week 39	10	56.54	0.45
	2-Mon week 40	10	56.74	0.93
296	3-Tue week 40	8	57.04	0.69
	4-Wed week 40	9	56.28	0.52
	5-Mon week 41	10	56.14	0.51

Table 24: Average melting peak areas of the heat treated sample **300** in different days.

JRC Code	day	replicates	Area J/g	SD J/g
	1-Wed week 39	10	56.64	0.61
	2-Mon week 40	10	56.50	0.30
300	3-Tue week 40	10	56.08	0.62
	4-Wed week 40	10	56.61	0.51
	5-Mon week 41	10	55.75	0.84

Table 25: Comparison of average melting peak areas of the heat treated sample **293** in different days.

JRC Code	day	F	F crit (95%)	SD	T	T crit (95%)	average
	1-2	1.39	4.03	=	3.503	2.101	≠**
	2-3	1.39	4.03	=	-3.960	2.101	≠**
	3-4	1.31	4.03	=	2.607	2.101	≠*
	4-5	4.80	4.03	≠	2.319	2.160	≠*
293	1-3	1.94	4.03	=	-1.058	2.101	=
	1-4	2.82	4.03	=	1.543	2.101	=
	1-5	1.70	4.03	=	5.791	2.110	≠**
	2-4	2.02	4.03	=	-1.171	2.101	=
	2-5	2.37	4.03	=	1.333	2.101	=
	3-5	3.31	4.03	=	5.727	2.145	≠**

Table 26: Comparison of average melting peak areas of the heat treated sample **296** in different days.

JRC Code	day	F	F crit (95%)	SD	T	T crit (95%)	average
	1-2	1.15	4.03	=	-1.039	2.101	=
	2-3	2.77	4.36	=	-1.132	2.120	=
	3-4	1.75	4.53	=	2.544	2.131	≠*
	4-5	1.05	4.10	=	0.607	2.110	=
296	1-3	-1.85	4.20	=	2.417	2.120	≠*
	1-4	1.14	4.43	=	1.377	2.120	=
	1-5	1.86	4.03	=	1.309	2.101	=
	2-4	2.11	4.43	=	1.579	2.110	=
	2-5	2.87	4.03	=	1.500	2.101	=
	3-5	3.16	4.20	=	1.847	2.120	=

Table 27: Comparison of average melting peak areas of the heat treated sample **300** in different days.

JRC Code	day	F	F crit (95%)	SD	T	T crit (95%)	average
	1-2	4.27	4.03	≠	0.649	2.160	=
	2-3	4.32	4.03	≠	1.929	2.160	=
	3-4	1.44	4.03	=	-2.075	2.101	=
	4-5	2.69	4.03	=	2.757	2.101	≠*
300	1-3	1.01	4.03	=	2.027	2.101	=
	1-4	1.43	4.03	=	0.122	2.101	=
	1-5	1.89	4.03	=	2.705	2.120	≠*
	2-4	2.99	4.03	=	-0.581	2.101	=
	2-5	8.06	4.03	≠	2.660	2.201	≠**
	3-5	1.86	4.03	=	1.011	2.101	=

Based on the generally good repeatability of the instrumental analysis and integration, the general mean of the peak areas for the 3 different samples were calculated and statistically compared (Tables 28 and 29).

Table 28: General mean of melting peak areas of the heat treated samples **293**, **296** and **300** analysed in different days.

JRC Code	replicates	Area J/g	SD J/g
293	50	60.39	0.91
296	47	56.53	0.69
300	50	56.31	0.68

Table 29: Comparison of average melting peak areas for the three groups of pure heat treated PTT.

JRC Code	F	F crit (95%)	SD	T	T crit (95%)	average
293-300	1,73	1,78	=	23.29	1.985	≠
293-296	1,82	1,76	≠	25.34	1.987	≠
296-300	1,05	1,77	=	1.569	1.985	=

On heat treated samples, statistics indicated that samples could be grouped in 2 different categories. In fact, sample **293** showed significant higher melting peak area when compared to the ones of both samples **296** and **300**.

The conclusion of all the mentioned experiments was that PTT samples were different in terms of melting peak area on the first heating cycle, independently if before the DSC analysis they were heat treated or not for 16 hours at 105 °C in a ventilated oven. Furthermore this difference could not be explained by a lack of repeatability of the DSC analysis and the peak integration.

In order to get a correct quantification of fibre mixtures containing PTT, it was then tested the approach to use, whenever possible, the same PTT and PET yarns of the fabric sample under evaluation (extracting them from the fabric) to build up the calibration curves used for quantification purposes. On the one hand, this approach showed two advantages: 1) to use, as standards for the calibration curve, yarns that had gone through the same thermal history of the sample under evaluation, thus showing the same degree of cristallinity; 2) to need just few milligrams of those standards. On the other hand, the same approach also showed two drawbacks: 1) the need of building up one calibration curve for each sample to be quantified; 2) the necessity to be able to manually separate at least some milligrams of pure PTT and PET from the samples under evaluation.

Table 30: Quantification with calibration curves built up with PTT and PET extracted from samples under evaluation.

JRC Code	Declared composition (PTT %)	Manual separation (PTT %)	DSC results (PTT%)(PTT-PET manually extracted)	Bias %	Calibration curve coefficient (m)	R^2
298	66	66.33	66.81	**-0.48**	0.6017	0.9952
302	65	74.14	74.81	**-0.67**	0.6198	0,9952
309	75	76.05	75.70	**0.35**	0.5841	0.9973
311	60	70.32	71.20	**-0.88**	0.5984	0.9955
312	60	62.99	62.74	**0.25**	0.5989	0.9946

As reported in Table 30, good correlation factors were obtained, ranging from 0.9946 to 0.9973. In addition, the quantification results of binary mixtures PTT/PET were in very good agreement with the reference ones obtained via manual separation. The differences, expressed in terms of bias (whose measurement unit is the same as for the content of PTT), are in all cases lower than 1%. Furthermore they were both positive

and negative, thus not showing a trend that could have being caused by a systematic error.

Based on the results of the five PTT/PET binary mixtures on which the approach was applicable, it could be concluded that an accurate quantification can be obtained using the DSC method integrating the melting peak of PTT on the first heating cycle and preparing the calibration curve with PTT and PET yarns manually extracted from the sample under evaluation.

6. 12th ENNETL meeting

The 12th Meeting of the European Network of National Experts on Textile Labelling was held on 30th November 2012 in Ispra. During the meeting, the JRC results regarding the analytical methods for the characterisation of DuPont's new fibre PTT were presented and discussed with the European national experts. The main conclusions and consensus about the results are reported in the following.

Regarding the characterisation of PTT, the microscopic analysis cannot be used to differentiate among the three types of polyester (PET, PTT and PBT); whereas FT-IR can distinguish among pure PTT, PET and PBT samples. On the basis of their melting points, DSC can discriminate between PTT and PET, but not between PTT and PBT. Even though PTT showed quite good elastic recovery, when measured at 25 % elongation, it could not be considered elastic essentially because of its moderated elongation at break (usually in the range 33 – 64 % elongation).

Concerning quantification, the usual pre-treatment described in the EU Regulation 1007/2011 can be applied to PTT and the value of zero for its *b* coefficient (mass loss during pre-treatment) was agreed. A consensus was also reached on the value 1.50 % as the agreed allowance of PTT. The comparison among quantitative results obtained by the JRC and DuPont using the manual separation method confirmed its high accuracy. The quantification of binary mixtures PTT/polyamide and PTT/wool obtained using methods 4 and 2, respectively, were considered to be in good accordance with the values obtained with manual separation, thus confirming the accuracy of those chemical methods. Experts considered not necessary to oragnise a validation exercise to establish *d* correction factors for PTT. The JRC will perform further analyses to reach 20 replicates for each chemical dissolution method and the obtained values will go directly into the Regulation.

Some additional work to be done by the JRC on the DSC method was also discussed and planned, such as 1) to study the influence of the cooling rate on the PTT's glass transition, cold crystallisation and melting point results, either by decreasing the rate (5 °C/min, 2.5 °C/min and 1 °/C) or increasing it (30 °C/min and 40 °C/min); 2) to study the influence of a quenching procedure using liquid nitrogen before the DSC analysis; 3) to investigate if a heat treatment of PTT samples at higher temperatures than 105 °C (130 °C and 150 °C) would erase the thermal history of the samples.

During the meeting it was also decided that a collaborative trial for the validation of the DSC method, if possible an improved version, will be necessary to allow its addition into the Textile Regulation. The JRC was entrusted to organise it.

It was decided that the validation will be performed on binary mixtures PTT/PET. Three manually separable samples at different levels of concentration and two not manually separable samples at two levels of concentration were chosen for the round robin test. Experts agreed to analyse 3 replicates for each level and built up calibration curves from the PTT and PET fibres extracted from each sample under evaluation in the cases where it is possible. In order to have validated reference values, laboratories will also be asked to perform manual separation of some specific samples and carry out all the pre-treatment for these samples in their own laboratories. The following Member States agreed to take part in the validation exercise: EL, IT, UK, CZ, LT, FR, PL and RO. The JRC will invite other laboratories, part of the ENNETL network, to take part in the exercise. Samples are planned to be sent by the end of January, with the analyses to be carried out during February and the evaluation of the results in March-April.

It was decided that the discussion concerning the name and the definition of this fibre would be held in the final ENNETL meeting, which will be organised in April-May, when all the final decisions will be taken.

7. Conclusions

The experimental work conducted at the JRC confirmed that test methods are available for the identification and quantification of the new fibre PTT when in mixtures with other fibres.

Regarding the identification, pure samples of PTT and other types of polyesters (PET and PBT) can be distinguished with Fourier Transform Infrared Spectroscopy (FT-IR), whereas the melting point determined by Differential Scanning Calorimetry (DSC) can be used to differentiate PTT from PET, but not from PBT. On the contrary, optical spectroscopy is not an adequate method to identify PTT, as it cannot be differentiated neither via longitudinal nor via cross-section view from the others polyesters. Solubility properties can be used only to confirm the polyester nature of the fibre. Even though, when measured at 25 % elongation, PTT showed quite good elastic recovery (82.3 - 87.6 %, corresponding to a permanent deformation of 6.2 - 8.8 %), the fibre could not be considered elastic essentially because of its moderated elongation at break (usually in the range 33 – 64 % elongation).

Concerning quantification, the pre-treatment described in the EU Regulation 1007/2011 is applicable to the new fibre. The agreed allowance of PTT and its correction factor for mass loss during pre-treatment were experimentally evaluated and the values, adopted by the network of national experts from Member States, are 1.50 % and 0 %, respectively.

The solubility properties of the new fibre were evaluated with all methods described in the EU Regulation 1007/2011 (except method 12 concerning the organic nitrogen content). The chemical dissolution methods 1-11, 13, 14 and 16 can be applied to mixtures containing PTT. The d correction factors measured by the JRC and DuPont were in good agreement. Experts judged that no validation was needed to establish these parameters for PTT and that the work performed by the JRC was sufficient. On the basis of JRC's work, PTT was completely insoluble in methods 1, 2, 3, 7 and 11 ($d = 1.00$) and could be considered insoluble in methods 4-6, 8-10, 13 and 16 ($d \leq 1.03$). It was partially soluble in method 15 ($d=1.05$) and completely soluble in method 14.

When feasible, manual separation was performed to quantify binary and ternary mixtures in order to determine reference values against which results obtained with

dissolution methods and DSC technique could be compared. The quantification results, obtained by the JRC and the petitioner, were in excellent agreement, confirming that the manual separation is a very accurate and reproducible method.

Binary mixtures of PTT/PET could not be quantified by any chemical methods, as the solubility properties of these two fibres are practically identical. The quantification of binary mixtures PTT/cotton and PTT/elastane was carried out with method 7; method 4 was used for the blends PTT/polyamide and method 2 for PTT/wool. In two cases, samples 306 and 322, the comparison between quantification done via manual separation and methods 4 and 2, respectively, could be made and a very good agreement was shown.

According to DSC analysis, various PTT samples gave different results in terms of melting peak area on the first heating cycle, independently if before the DSC analysis they were heat treated in a ventilated oven (for 16 hours at 105 °C), in order to erase their thermal history, or not. This difference was not due to a lack of repeatability of the DSC analysis and the peak integration. This is most probably the reason why the quantification of PTT in binary mixtures did not give acceptable results when the calibration curves were built up with fibres not directly extracted from the samples under investigation, before or after heat treatment. In fact, the bias, calculated against the reference values obtained via manual separation, was usually higher than 1% (the maximum value was 12.83 %). On the contrary, the quantification results of binary mixtures PTT/PET, obtained using calibration curves built up with PTT and PET manually extracted from the sample under evaluation, were in very good agreement with the reference ones obtained through manual separation. In fact, the differences expressed in terms of bias were in all cases lower than 1%. In these conditions, the DSC method could be judged accurate.

During the 12th ENNETL meeting, experts suggested to perform further experimentation to try to develop an accurate DSC method that does not need the extraction of PTT and PET yarns from the sample under evaluation to build up the calibration curve. To this aim they suggested to study the influence of the cooling rate and of the quenching with liquid nitrogen on the PTT's glass transition, cold crystallisation and melting point. The JRC will also investigate if the heat treatment of PTT samples at higher temperatures (130 °C and 150 °C) is effective to erase the thermal history of the samples in order to have the same degree of crystallinity in each sample before analysis them with DSC.

A consensus was reached on the need to validate the new, if possible improved, DSC quantification method to be added to the Textile Regulation. Consequently, the JRC was entrusted to organise a collaborative trial at European level according to ISO 5725:1994.

The discussion concerning the name and the definition of this fibre would be held in the final ENNETL meeting, which will be organised in April-May 2013.

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Abstract

In November 2011, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise to verify the validity and applicability of the testing methods, proposed by DuPont, for the identification and quantification of their new fibre polytrimethylene terephthalate (PTT). The fibre is a type of polyester that differs from the common one polyethylene terephthalate (PET) as it contains one more methylene group in the aliphatic chain that links the terephthalic moiety.
Experimental results confirmed that PTT identification can be achieved using Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC). FT-IR can distinguish among the three types of polyester PTT, Pet and polybutylene terephthalate (PBT), whereas DSC can differentiate only between PTT and PET on the basis of their melting points.
For quantification purposes, the normal pre-treatment described in the EU Regulation 1007/2011, was proved to be applicable to PTT and its correction factor b for mass loss during pre-treatment was established (0 %). The agreed allowance of the new fibre was measured (0.34 %). The European network of national experts on Textile Labelling (ENNETL) established the value of 1.50 % for PTT agreed allowance, for consistency with the already established values for polyester and elastomultiester. The solubility properties of PTT were evaluated with all methods described in EU Regulation 1007/2011, with the exception of method 12. The new fibre was insoluble in methods 1-11, 13 and 16. The d correction factors were established on the basis of the experimental work carried out by the JRC. The resulting values were: 1.00 for methods 1, 2, 3, 7 and 11, 1.01 for methods 4, 5, 9 and 10, 1.02 for method 13 and 1.03 for methods 6, 8 and 16. PTT was completely soluble in method 14, whereas it was partially soluble in method 15 that consequently cannot be used in the quantification of blends containing PTT.
For the quantification of PTT in binary mixtures, manual separation is an adequate technique, whenever applicable. The following chemical dissolution methods can also be used: 1-11, 13, 14 and 16.
The quantification results of binary mixtures PTT/PET obtained by DSC method, using calibration curves built up with PTT and PET manually extracted from the sample under evaluation, were in very good agreement with the reference ones obtained through manual separation. In fact, the differences expressed in terms of bias were in all cases lower than 1%. In these conditions, the DSC method could be judged accurate.
A consensus among the members of ENNETL was reached on the need to validate the new, if possible improved, DSC quantification method to be added to the Textile Regulation. Consequently, the JRC was entrusted to organise the validation exercise at European level according to ISO 5725:1994. The discussion concerning the name and the definition of this fibre would be held in the final ENNETL meeting, which will be organised in April-May 2013.

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